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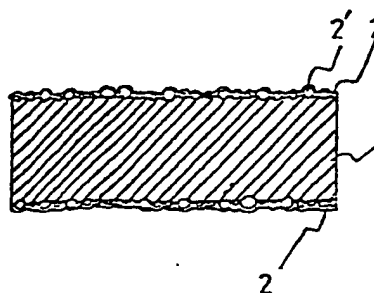
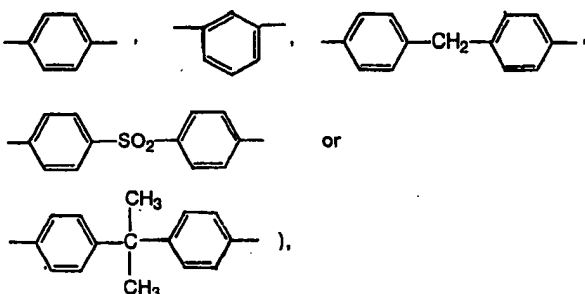
(54) **Polyester laminated film.**

(57) The present invention provides a polyester laminated film which comprises a transparent layer (1) and a delustered layer (2) laminated at least on one side face of the transparent layer. The transparent layer is formed by a biaxially stretched polyester film mainly composed of polyethylene terephthalate, while the delustered layer is made of an at least uniaxially stretched polyester film which is mainly composed of a polyethylene terephthalate copolymer containing, as a copolymer composition, 1 to 20 mol.% of the delustered layer of

and which also contains inert inorganic particles (2') of 0.3 to 20 microns diameter in an amount 3 to 40% by weight of the delustered layer.

Film according to the present invention as described above is roughened on the surface, and has excellent writability and transcribability by pencils, ink, Indian ink, etc., combined with an excellent transparency, and therefore, is very useful for use as tracing films and the like.

$$\text{H} - \text{OCH}_2\text{CH}_2 - \text{O} - \text{X} - \text{O} - \text{CH}_2\text{CH}_2 - \text{O} - \text{H}$$
 (wherein n is an integer from 2 to 140, and X represents



POLYESTER LAMINATED FILM.

The present invention relates to a polyester composite or laminated film (referred to as a polyester laminated film hereinbelow) which comprises at least one delustered layer and a transparent layer.

5           It should be particularly noted that the present invention relates to a laminated film superior in transparency, in which the transparency thereof is not reduced despite the fact that its surface is sufficiently roughened.

          Conventionally, there have been widely employed  
10 various kinds of tracing films produced by roughening the surface of an oriented polyethylene terephthalate film so as to be superior in writing ability (referred to as writability hereinbelow) and transcribability by pencils, ink, indian ink, etc., and moreover, capable of observing  
15 written items, printed matter, etc. placed at the back of said film through the surface thereof.

          For example, in U.S. Patent No.4 067 855, there is disclosed a biaxially oriented polyester film which contains 0.2 to 3.0% by weight of "reactive particles" consisting of  
20 lithium and phosphorus as a lithium salt of phosphoric acid ester constituent of short chain polyesters.

          Meanwhile, in Japanese Patent Publication No.31908/1978, there is also disclosed a delustered polyester film which is produced by uniaxially or biaxially  
25 orienting a saturated linear polyester which contains 0.5

to 30% by weight of glass fibres having fibre length shorter than 0.5 mm and fibre length/fibre diameter larger than 5.

In the known films as described above, however,  
5 there have been disadvantages in that, since it is necessary for the films to contain a large amount of particles in order to increase the surface roughness, the resultant films become undesirably opaque, while films superior in writability and delustering cannot be obtained, if the  
10 amount of particles contained therein is excessively small.

In British Patent No.1 096 064, there is also disclosed a laminated film which contains an inert additive in the outermost layer. In the above conventional film, however, there have still been drawbacks such as described  
15 hereinbelow:

(1) Even when a large amount of inert particles is added to the outermost layer, the surface undulation or unevenness during stretching is not sufficiently deep, and therefore, favourable delustering effect as in the sandblast process  
20 is not available.

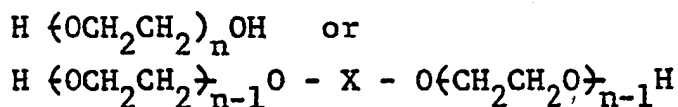
(2) Moreover, as the amount of addition is increased, the film becomes undesirably cloudy so as to be opaque.

(3) Meanwhile, if the delustered layer is thickened or the amount of addition of inert particles is increased for  
25 the improvement of the delustering effect, stretching ratio is limited by breakage or tearing during stretching, and thus films superior in mechanical properties are not available.

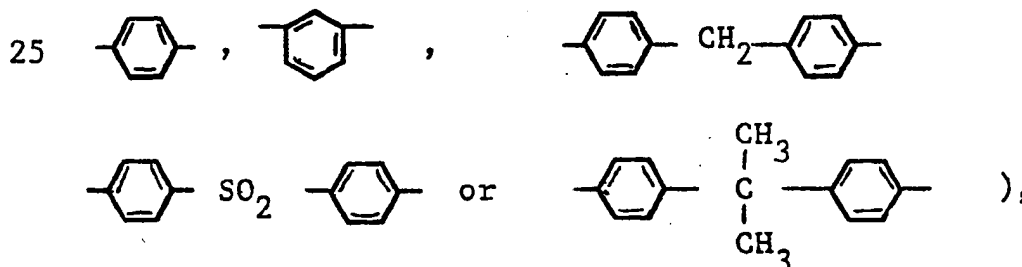
Accordingly, it is a primary object of the present invention to provide a polyester laminated film superior in surface delustering quality and transparency, with favourable mechanical properties peculiar to the polyethylene terephthalate film being sufficiently maintained, through elimination of disadvantages inherent in the conventional films of this type.

It is another particular object of the present invention to provide a polyester laminated film of the above described type which has but small reduction of transparency, while having a large delustered effect and superior writability.

According to the present invention there is provided an improved laminated film which comprises a transparent layer and a delustered layer laminated at least on one side face of said transparent layer. The transparent layer comprises a biaxially stretched polyester film mainly composed of polyethylene terephthalate. The delustered layer comprises an at least uniaxially stretched polyester film which is mainly composed of a polyethylene terephthalate copolymer containing as a copolymer composition, 1 to 20 mol. % of



(wherein n is an integer from 2 to 140, and X represents



and which also contains inert inorganic particles of 0.3 to 20 microns average diameter in an amount of 3 to 40% by weight.

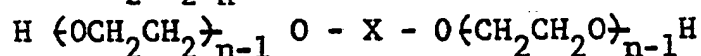
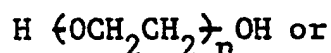
The laminates of the present invention in general  
5 have a gloss of less than 15% and more preferably, of less than 10% based on the method of JIS-Z-8741, and transparency with total light or luminous transmission ratio higher than 60% as measured by the method of JIS-K-6714.

In the accompanying drawing, Fig. 1 is a fragment-  
10 ary side sectional view showing, on an enlarged scale, a polyester laminated film according to one preferred embodiment of the present invention, in which delustered layers are provided on opposite surfaces of a transparent layer.

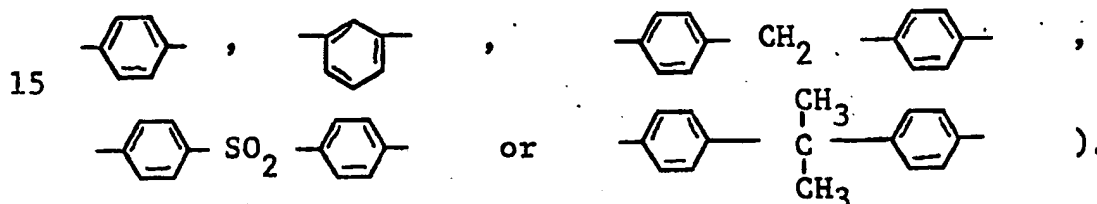
The transparent layer referred to in the present  
15 invention is of a polyester which is constituted by a repetition unit mainly composed of ethylene terephthalate, in which it is desirable that the ethylene terephthalate unit thereof occupies more than 98 mol. % and more preferably, more than 99 mol. % in said polyester, and that the  
20 degree of polymerization of the polyester to be employed should be such that the intrinsic viscosity of its ortho-chlorophenol solution at 25°C is higher than 0.45 and more preferably, higher than 0.60. If the ethylene terephthalate unit is less than 98 mol. %, with an intrinsic viscosity  
25 of less than 0.45, the mechanical properties inherent in the polyethylene terephthalate cannot be fully developed. In connection with the above, a polyethylene terephthalate homopolymer is particularly preferable.

Although it is desirable that other impurities should not be mixed into the polyethylene terephthalate constituting the transparent layer, catalysts, catalyst residue, and other additives, etc. may be mixed to such an extent as will not impair the transparency.

On the other hand, the delustered layer referred to in the present invention is constituted by the ethylene terephthalate copolymer repetition unit, and contains, in its main chain, 1 to 20 mol. % and more preferably, 1.5 to 10 mol. % of



(wherein n is an integer from 2 to 140, and X represents



For example, there may be employed diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol with molecular weight of less than 6000, or ethylene oxide adduct of hydroquinone, ethylene oxide adduct of resorcinol, ethylene oxide adduct of 2,2'-di(4 hydroxyphenyl) propane, or ethylene oxide adduct of 2,2'-di(4 hydroxyphenyl)sulphone. In the case where the content of such copolymer composition is less than 1 mol. %, the transparency is deteriorated, while if the content exceeds 20 mol. %, the mechanical properties of the laminated film become inferior. More preferably, the optimum content of the copolymer composition is in the range of 1.5 to 10 mol. %.

It should be noted here that, although copolymer chains other than the ethylene terephthalate chain may be contained in the main chain of the transparent layer in an amount within 2 mol. %, it is usually necessary for obtaining a transparent film, that the copolymer chain to be contained in the main chain of the delustered layer should be larger in amount than the copolymer chain contained in said main chain for the transparent layer.

The delustered layer according to the present invention contains inert inorganic particles having average diameters in the range of 0.3 to 20 microns, and more preferably, of 3 to 15 microns, in an amount of 3 to 40% by weight and more preferably, of 4 to 20% by weight. For the inert inorganic particles, there may be favourably employed silica, kaolin, talc, silica alumina, zinc oxide, zinc sulphide, barium oxide, barium sulphate, zirconium oxide, calcium carbonate, titanium oxide, etc. In other words, for the inert inorganic particles, any particles of inorganic compounds which will not react with the polyester used for the delustered layer may be employed, but normally solid particles of inorganic oxides or inorganic salts which do not react with said polyester are employed. In the case where the particle diameters of such inert inorganic particles are smaller than those in the range earlier described, if the amount of addition thereof is small, the delustering on the surface becomes inferior, and a delustered film with gloss of less than 15% cannot be obtained. Meanwhile, if the particle diameter is

excessively large, it is difficult to render the delustered layer sufficiently thin, thus resulting in a difficulty in the improvement of the transparency. On the other hand, if the amount of addition is too large, the transparency  
5 is also impaired.

The copolymerized polyester in which the inert inorganic particles as described above are added to a large amount may be produced by the normal condensation polymerization process. Particularly when a large amount  
10 of inert inorganic particles are added, it is difficult to obtain polyesters of high molecular weight due to a problem related to excessive viscosity, but by copolymerization as in the present invention, reduction in viscosity is advantageously achieved. Meanwhile, it is possible to  
15 uniformly disperse inorganic particles into the copolymerized polyester in a separate process through blending, kneading and extrusion. Moreover the master batch method can also be effectively utilized.

The lamination thickness ratio of the delustered  
20 film B to be laminated at least on one side face of the transparent layer A employed in the present invention, may be suitably selected according to end uses. For improving the transparency, the thickness of the delustered layer may be as thin as possible. However, if it becomes too  
25 thin, uniform distribution with respect to the inert particles is not readily achieved. The thickness of the delustered layer should desirably be in the range of 1 to 20 microns and more preferably, of 3 to 10 microns per one side face. As shown in a schematic cross section of



Fig. 1, it is desirable that particles with diameters of 3 to 15 microns are aligned uniformly in one layer to form a delustered layer with gloss less than 15%.

It is to be noted that the thickness of the delustered layer indicates the average thickness including the fine particles in the delustered layer, as obtained through measurement of the cross section of the laminated film by an optical microscope.

The thickness of the transparent layer may also be properly selected according to the end uses, and is normally chosen from the range between 10 and 200 microns and more preferably, between 15 and 150 microns.

Referring now to the drawing, the laminated film according to the present invention will be explained in detail hereinbelow.

In Fig. 1, there is shown one example in which delustered layers 2 are laminated on opposite side faces of a transparent layer 1, with inert inorganic particles being represented by the numeral 2'.

Although the polyethylene terephthalate polymer and copolymer can be formed into an unstretched film by the ordinary polyester film forming process, for example, by T-die method, inflation method, etc., it may be so arranged that the transparent layer and delustered layer are formed by lamination extrusion through a simultaneous extrusion process, or the unstretched film laminate may be obtained by lamination immediately after separate extrusion from independent dies, and the laminated unstretched film

thus obtained can further be subjected to stretching. Furthermore, it is also possible to stretch the laminated film in a direction at right angles with the uniaxial stretching direction of the transparent layer after extruding the delustered layer onto the uniaxially stretched film for forming the transparent layer of the present invention.

The delustering effect according to the present invention is effectively developed by the film as obtained by biaxially stretching the transparent layer of the laminated unstretched film, and also by at least uniaxially stretching the delustered layer thereof. More specifically, although the delustered layer has no particular delustering effect in the unstretched film, a delustered surface with gloss of less than 15% is obtained only through the uniaxial stretching or biaxial stretching effected as described above. It is to be noted that subjection to the biaxial stretching is particularly preferable.

For best overall results among the delustering, transparency and mechanical properties by the stretching, the stretching temperature, stretching ratio, and heat treating temperature may be suitably selected. The stretching conditions and heat treatment conditions may be generally the same as in the case of an ordinary polyethylene terephthalate film, but in the delustered layer containing copolymer according to the present invention, the stretching can be effected at higher temperatures or the heat treatment may also be conducted at higher temperatures. It is to be noted that such high temperature as

will melt the copolymer of the delustered layer is unsuitable, and therefore, should be avoided. Normally, a stretching temperature in the range of 80 to 150°C and heat treating temperature in the range of 150 to 245°C are employed. Although the stretching ratio is not particularly restricted, it should normally be approximately 2.5 to 6 times and more preferably, 2.5 to 4 times in the longitudinal direction and lateral direction. For the stretching method, various known processes may be employed.

It is needless to say that stretching processes such as multi-stage stretching, second longitudinal stretching, etc. may be applied. A non-stretched film or a film with a low stretching ratio lacks favourable mechanical properties and utility as a writing film, while the delustering effect of the present invention as described earlier is not readily displayed. It may be noted that, in the case of a single layered film consisting only of the delustered layer, breakage of film may take place upon increasing the stretching ratio, but in the laminate film of the present invention, it becomes possible to adopt a high stretching ratio, while the favourable delustering effect and good mechanical properties can be simultaneously achieved.

By the stretching, orientations are developed both in the delustered layer and transparent layer. In the orientation of the delustered layer, the absolute value  $|\Delta n|$  of the birefringence should preferably be higher than 0.004. In the case of non-orientation, resistance to solvents is reduced, and depending on the

kinds of solvents contained in ink or the like, the delustered layer may be eroded, or the film tends to be subjected to scratches when writing is effected by a hard pencil.

5 For maintaining a sufficient mechanical strength and stiffness, it is desirable that the transparent layer should be biaxially oriented, and should normally have the absolute value of birefringence  $|\Delta n|$  in the range of 0.004 to 0.2.

10 The delustered layer is opaque as compared with the transparent layer, and its opacity is further increased by the stretching, when the amount of addition of the inert inorganic particles becomes large. Furthermore, in cases where stretching is effected at high temperatures for the  
15 improvement of stretching ratio, or heat treatment is carried out at high temperatures for the improvement of the dimensional stability of the stretched film, the delustered layer becomes still more opaque. It is to be noted that the main feature of the present invention resides in  
20 that, by employing a polyester which contains, as the copolymer composition,

$H(OCH_2CH_2)_nOH$  or  $H(OCH_2CH_2)_{n-1}O-X-O(CH_2CH_2)_{n-1}H$  in

the delustered layer, together with the inert particles which develop the delustering effect, the above disadvantages related to the reduction of transparency have been  
25 simultaneously eliminated by a single effort. Particularly, when the ratio of the copolymer composition in the polyester constituting the delustered layer is increased, the transparency is improved by the stretching, with a sufficient

transparency being maintained even in the case of high temperature stretching or high temperature heat treatment. Moreover, since the delustered layer is laminated with the transparent layer, it is also possible to keep the thickness  
5 of the delustered layer at a low level so as to decrease the reduction in physical properties, with a further improvement of the apparent transparency. In actual use, it is desirable to provide a total luminous transmission ratio of more than 60% in the case where the overall thickness  
10 is 100 $\mu$ .

The adhesion property between the transparent layer film A and the delustered layer film B is good, and in the case of stretching after formation into a laminated film by the simultaneous extrusion process or when the stretch-  
15 ing is effected after extrusion of the delustered layer onto the unstretched film of the transparent layer for the lamination, or in the case of stretching after extrusion of the delustered layer onto a uniaxially stretched film for the transparent layer film, etc., sufficient adhesion  
20 is achieved in any of the above cases, and a strong adhesive strength is achieved without requiring any bonding agent. In connection with the above, it is to be noted that favourable adhesion may also be achieved even in a two-layered laminated film composed of A/B layers, a three-  
25 layered laminated film composed of B/A/B layers, or a multi-layered laminated film composed of more layers.

It should be further noted that proper anti-oxidants, ultra-violet absorbers, pigments, additives such as dyes, or other additives may be simultaneously employed for the transparent layer and/or the delustered layer within a range which will not impair the particular characteristics of the present invention.

The delustered polyester laminated film according to the present invention has particular features as described hereinbelow, so that the disadvantages of the conventional films may be eliminated;

(1) Since the surface is roughened to have gloss of less than 15%, the writability thereof by pencils, ink, indian ink, etc. is extremely high.

(2) The laminated film of the present invention has a superior transparency which allows written items, printed matter, etc. placed behind it to be readily observed there-through for easy tracing, and allows a clear and definite copy of the original document.

(3) The laminated film according to the present invention can be manufactured merely through the film forming process at high productivity and low cost, without passing through any additional conversion processes.

(4) Even with high stretching ratio, high temperature stretching and high temperature heat treatment, films maintaining a sufficient transparency and superior mechanical properties may be obtained.

(5) The adhesion between the transparent layer and the delustered layer is extremely favourable, and there is no drawback of separation or peeling off at the boundary faces therebetween.

The polyester laminated delustered film of the present invention can also be used for decorations, labelling, hot stamping and packing, through application of printing, metal deposition or the like, besides its normal use for transcribing films such as tracing film, drafting film and copying film.

It should further be noted that an anion anti-static agent may be added to the delustered layer according to the present invention. For the antistatic agent as referred to above, salts containing sodium, potassium and copper anion, may be favourable employed. More specifically, there may be employed fatty acid salts, higher alcohol sulphate ester salts, aliphatic alcohol phosphate ester salts, sulphonates of dibasic fatty acid esters, alkylaryl sulphonates, formalin condensation naphthalene sulphonates, polyethylene glycol ether sulphate ester salts or halogeno-salts, and the amount of addition thereof should preferably be in the range of 0.1 to 10% by weight. If the amount is less than the above, the anti-static effect is not sufficiently developed, while on the contrary, if it exceeds the above range, defects such as bleeding-out onto the surface layer, may take place. As the antistatic agent, sodium dodecylbenzene sulphonate is particularly preferable.

By the addition of the antistatic agent as described above, there is the advantage that workability is improved during handling either as a continuous film or leaf or sheet films, for example, in feeding continuous film into an automatic drawing machine or supplying sheet films into a sheeting type drawing machine.

Hereinbelow, Examples are inserted for the purpose of illustrating the present invention, without any intention of limiting the scope thereof. It is to be noted that in the Examples to be described hereinafter, every "part" is  
5 represented on the basis of weight.

The measuring methods for the characteristic values according to the present invention are as follows.

- (1) Transparency: Based on the method of JIS-K-6714.
- (2) Gloss : Measurements were taken on 60 degree  
10 specular gloss based on the method of JIS-Z-8741 for judging the degree of delustering.
- (3) Pencil writability -  
Lines were drawn with pencils of 2B to 8H in hardness, and after copying by a "U-BIX" (Copier made by Konisiroku Co.), clarity and definiteness of the lines were  
15 evaluated.
- (4) Ink writability -  
Lines were drawn by oil ink for an automatic drawing machine, and after copying by "U-BIX", clarity and  
20 definiteness of the lines were evaluated with 5 points set as a full mark.

#### EXAMPLE 1.

Dimethyl terephthalate was subjected to an ester exchange reaction with ethylene glycol in the presence of  
25 a catalyst of manganese acetate at 0.04% (by weight), and, after addition of 0.03% (by weight) of trimethyl phosphate as an anti-colouring agent, caused to flow down into a polymerizing kettle so as to be subjected to polymerization reaction under a state of high vacuum at 280°C through



addition thereto of 0.03% of  $\text{Sb}_2\text{O}_3$  as a polymerizing catalyst, and thus polyester polymer for the transparent layer was obtained.

Meanwhile, after the ester exchange reaction in  
5 the similar polymerizing process as above, 6 mol. % of ethylene oxide adduct of bisphenol A was added to the final polymer with addition of 5% by weight of "Syloid 72" (Trade name of Fuji Devison Co.)(wet process  $\text{SiO}_2$ , average particle diameter 4 microns) dispersed in a slurry into  
10 ethylene glycol for further polymerization reaction under a high vacuum, and thus the polyester polymer for the delustered layer was obtained.

After separately subjecting both of the above polymers to vacuum drying at  $170^\circ\text{C}$ , the resultant polymers  
15 were further subjected to composite extrusion by a simultaneous extruder to provide the structure of delustered layer/transparent layer/ delustered layer, and the sheets thus obtained were subjected to simultaneous stretching both in the longitudinal and lateral directions at a stretching ratio of 3.3 times.  
20

The resultant film thus obtained had a structure in which each of the delustered layers on the surface was 6 microns thick, and the transparent layer was 88 microns thick, while the intrinsic viscosity [IV] of the transparent  
25 layer was 0.65 and the intrinsic viscosity [IV] of the delustered layer was 0.615. Meanwhile,  $|\Delta n|$  for the transparent layer was 0.022, and  $|\Delta n|$  of the delustered layers was 0.010.

The resultant film as described above had a gloss of 8.5% in the 60 degree direction, and yet was sufficiently transparent, with the total luminous transmission ratio at 80%. Upon drawing with pencils respectively of 2B and 8H in hardness, it was found possible to draw with pencils of 4H to 2B in hardness, and when diazo copies were taken by the film drawn in the above described manner as an original, their clarity and definiteness were sufficiently legible. Moreover upon drawing of lines by the oil ink to be employed for an automatic drawing machine, clear and definite lines could be formed.

#### EXAMPLE 2.

In a similar method as in Example 1 except for the alterations in the amount of the "Syloid 72" to 3% (by weight) as the additive for the delustered layer, with addition of anatase type  $\text{TiO}_2$ , (average particle diameter  $5\mu$ ) at 20% (by weight), a laminated film composed of delustered layer/transparent layer/delustered layer was obtained. The gloss thereof was 9.2% with writability or drawability by pencils ranging from 5H to 2B in hardness. Meanwhile, the total luminous transmission ratio could be improved from 64% with the thickness of the delustered layer at 6 microns, to 72% at a thickness of 5 microns, and to 79% at a thickness of 4 microns. The intrinsic viscosity [IV] of the transparent layer was 0.65, with  $|\Delta n|$  of 0.023, while the intrinsic viscosity [IV] of the delustered layer was 0.615, with  $|\Delta n|$  of 0.012.

## EXAMPLE 3.

In a similar method as in Example 1, the copolymer composition for the delustered layer was altered from ethylene oxide adduct of bisphenyl A to polyethylene glycol with molecular weight of 1000. The luminous transmission ratio of the three-layered laminated film thus obtained was 82%, with the gloss at 7.7%. In the writability or drawability test with pencils, drawing was effected with pencils of 4H to 2B in hardness. The intrinsic viscosity [IV] for the transparent layer was 0.65, with  $|\Delta n|$  of 0.023, while the intrinsic viscosity [IV] for the delustered layer was 0.615, with  $|\Delta n|$  of 0.008.

## EXAMPLE 4.

In a similar method as in Example 1, a three-layered laminated film composed of the delustered layer/transparent layer/delustered layer was prepared. Table 1 shows the compositions and characteristics of the resultant film. In Table 1, the experiments Nos.1 to 4 relate to the structure according to the present invention, each of which shows a good film forming characteristic, with simultaneous favourable transparency and delustering characteristic. These films are also superior in pencil writability and ink writability.

Experiments Nos.5 to 9 show comparative embodiments, in which it is noticed that frequent breakages take place in the single-layered film with adequate delustering agent whilst an insufficient amount of addition of the delustering agent results in inferior pencil writability and ink writability. From experiment No.8, it is seen that in laminated

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- 19 -

film where the delustered layer does not contain copolymer composition, the delustering effect is insufficient, with inferior transparency.

TABLE I

Thickness of transparent parent layer(μ)	Delustered layer				Film forming ability	Gloss (%)	Total luminous trans-mission ratio(%)	Pencil writability	Ink writability	Transparent layer		Delustered layer	
	Total thickness for front and back sides (μ)	Copolymer composition		Delustering agent content (weight %)						IV	Δn	IV	Δn
		Compound	Content (mol. %)										
90	10	PEG	5	7	Favorable	8.2	81	5H	5	0.65	0.020	0.615	0.007
87	13	PEG	5	7	Favorable	7.2	75	5H	5	0.65	0.020	0.615	0.007
90	10	TEG	5	7	Favorable	8.8	73	5H	5	0.65	0.024	0.615	0.014
90	10	PEG	3	5	Favorable	9.3	80	4H	5	0.65	0.020	0.615	0.008
0	100	-	0	7	Frequent breakage	10.2	3	4H	2	-	-	0.615	0.01
0	100	-	0	2.5	Favorable	37	12	2H	1	-	-	0.615	0.004
0	100	PEG	3	7	Frequent breakage	8.6	5	5H	5	-	-	0.615	0.002
90	10	-	0	7	Favorable	11.2	58	4H	3	0.65	0.028	0.615	0.013
90	10	PEG	3	2.5	Favorable	30	76	2H	2	0.65	0.020	0.615	0.008

(Note) PEG: Polyethylene glycol with molecular weight 1000

TEG: Triethylene glycol

## EXAMPLE 5

Dimethyl terephthalate was subjected to ester exchange reaction with ethylene glycol in the presence of a catalyst of manganese acetate at 0.04% (by weight), and 5 0.023% (by weight) of monomethyl phosphate as an anti-colouring agent, 4% (by weight) of polyethylene glycol with molecular weight 2000, and 5% (by weight) of wet process  $\text{SiO}_2$  with average particle diameter of 5 microns were added thereto, while 2% (by weight) of sodium dodecyl-benzene 10 sulphonate was added as an anti-static agent, with further addition of 0.025% by weight of  $\text{Sb}_2\text{O}_3$  as a polymerizing catalyst for subsequent polymerization reaction under a high vacuum state at  $280^\circ\text{C}$ . As a result, polyethylene glycol copolymerized polyethylene terephthalate with inher- 15 ent viscosity of 0.62 was obtained, and this resin was used for the delustered layer.

On the other hand, dimethyl terephthalate was subjected to ester exchange reaction with ethylene glycol in the presence of 0.04% (by weight) of manganese acetate cata- 20 lyst, and after addition of 0.023% (by weight) of monomethyl phosphate thereto, caused to flow into the polymerizing kettle for polymerization reaction under a high vacuum state at  $280^\circ\text{C}$  through employment of 0.03% (by weight) of  $\text{Sb}_2\text{O}_3$  as a catalyst. As a result, polyethylene terephthal- 25 ate with inherent viscosity of 0.65 was obtained, and this resin was used for the transparent layer.

After separately subjecting both of the above resins to vacuum drying at  $170^\circ\text{C}$ , the resultant material was co-extruded to form three-layered composite film viz.

delustered layer/transparent layer/delustered layer in a thickness ratio of 5/90/5. The sheet thus obtained was longitudinally stretched for 3.0 times at 95°C, with a further stretching in the lateral direction for 3.5 times  
5 by a clip tenter at 125°C for subsequent heat setting at 205°C. The resultant three-layered laminated film thus obtained had delustered layers each of 5 microns formed on the front and back faces of a transparent central layer of 90 microns. The value of  $|\Delta n|$  for the transparent layer  
10 was 0.042, while  $|\Delta n|$  for the delustered layer was 0.018. The above film had a gloss of 9.2% in the 60 degree direction, and a superior delustering ability equivalent to a sandblast film, and was excellent in pencil writability and also in drawability by automatic drawing machine ink. Furthermore  
15 the film as described above had a total luminous transmission ratio of 79% and a surface resistivity of  $2 \times 10^{11} \Omega$ , and was superior in transparency and anti-static characteristics. Upon trial feeding into an automatic drawing machine through application of perforation processing to the film, worka-  
20 bility and drawability equivalent to those in the sandblast film were achieved. When three sheets of the above film were piled up one upon another for taking diazo copies, the film of the embodiment provided a clear and definite copy, whereas in the sandblast film, the drawing at the  
25 upper portion of the piled up film was indefinite.

## EXAMPLE 6

After separately subjection copolymer [I] of polyethylene terephthalate including polyethylene glycol as a copolymerizing component and containing the wet process

5  $\text{SiO}_2$  as obtained in Example 5 and polyethylene terephthalate resin [II] to vacuum drying at  $170^\circ\text{C}$ , the material was further subjected to composite extrusion by a two-layered co-extruder to form a delustered layer/transparent layer laminate with a thickness ratio of 7/93. The sheet thus obtained

10 was subsequently subjected to roll stretching for 2.9 times in the longitudinal direction at  $95^\circ\text{C}$  and further, to stretching for 3.6 times in the lateral direction by a clip tenter at  $130^\circ\text{C}$ , with subsequent heat setting at  $210^\circ\text{C}$ . The two-layered laminated film thus obtained consisted of a

15 rear transparent layer (IV at 0.65,  $|\Delta n|$  at 0.041) of 93 microns in thickness, and a delustered layer (IV at 0.62,  $|\Delta n|$  at 0.022) of 7 microns in thickness in front. The gloss of the delustered layer in the 60 degree direction was 8.8%, while the delustering ability thereof was as good as that of

20 sandblast items, while the film was also superior in writability by pencils in the range of 5H to 2B in hardness, and also in drawability for automatic drawing machine ink. Said film is similarly superior in transparency, with a total luminous transmission ratio of 81%. Upon trial use for the

25 automatic drawing machine through application of perforating processing thereto, the film showed the same workability and drawability as the sandblast items.



## EXAMPLE 7

The polyethylene terephthalate resin [II] as obtained in Example 5 was dried, and extruded into a film of 1200 microns in thickness by the extruder, and subsequently  
5 subjected to roll stretching for 3.2 times in the longitudinal direction at 95°C. Onto the uniaxially stretched film thus obtained, polyethylene terephthalate copolymer [I] including polyethylene glycol as a copolymerising component and containing the wet process SiO<sub>2</sub> was melt-extruded to  
10 achieve a thickness ratio of 5/95, with subsequent stretching for 3.6 times at 130°C in the lateral direction, and heat setting at 205°C. The two-layered laminated film thus obtained consisted of a rear transparent layer (IV: 0.65, |Δn| : 0.038) of 95 microns, and a delustered layer (IV:  
15 0.615, |Δn| : 0.065) of 5 microns in thickness in front. The gloss of the delustered layer in the 60 degree direction was 9.5%, and the film was superior in writability by pencils of 4H to 2B in hardness, and also in drawability by ink for an automatic drawing machine. Said film had a total luminous  
20 transmission ratio of 82%, and upon printing of a section composed of longitudinal and lateral lines on the transparent layer, those lines could be seen through the opposite delustered layer.

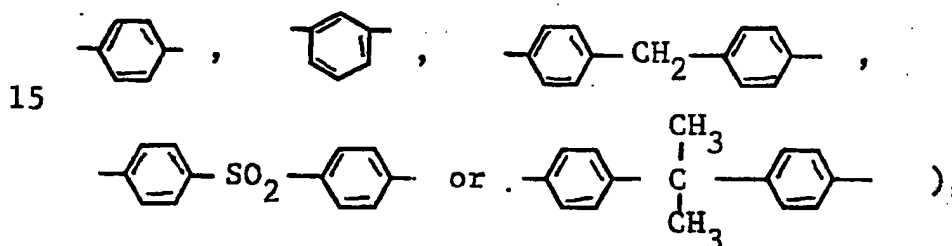
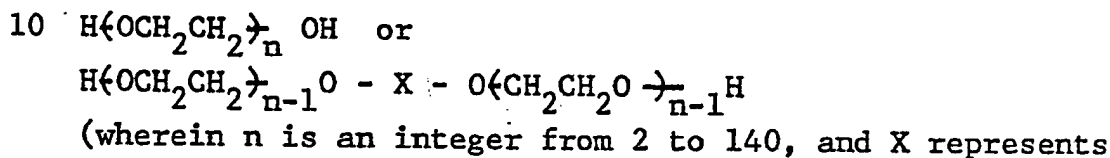
## EXAMPLE 8

25 As a polyester polymer for the delustered layer in Example 1, a polymer was prepared in which, instead of the ethylene oxide adduct of bisphenol A, 4 mol. % of bis-hydroxyethyl hydroquinone was copolymerized with respect to the final polymer. By employing the above polymer as a

delustered layer, the material was subjected to composite extrusion by the co-extruder in the similar manner as in Example 1, and the sheet thus obtained was subjected to simultaneous stretching for 3.3 times both in the longitudinal and lateral directions at 98°C. The resultant film had such a construction in thickness that the ratio of the delustered layer/transparent layer/delustered layer was 6/88/6 microns (the transparent layer IV: 0.65,  $|\Delta n|$  : 0.022, the delustered layers IV : 0.65,  $|\Delta n|$  : 0.008). The above film had a gloss in the 60 degree direction of 8.8%, and was superior in delustering ability, and moreover sufficiently transparent, with a total luminous transmission ratio of 74%.

## CLAIMS :

1. A polyester laminated film which comprises a transparent layer and a delustered layer laminated at least on one side face of said transparent layer, said transparent layer comprising a biaxially stretched polyester film
- 5 mainly composed of polyethylene terephthalate, said delustered layer comprising an at least uniaxially stretched polyester film which is mainly composed of a polyethylene terephthalate copolymer containing, as a copolymer composition, 1 to 20 mol. %



- and which also contains inert inorganic particles of 0.3 to 20 microns average diameter in an amount 3 to 40% by
- 20 weight of said delustered layer.

2. A polyester laminated film according to Claim 1, wherein said inert inorganic particles have an average particle diameter in the range of 3 to 15 microns.

3. A polyester laminated film according to Claim 1 or

25 Claim 2 wherein the amount of said inert inorganic particles in the delustered layer is in the range of 4 to 20% by weight of said delustered layer.

4. A polyester laminated film according to any one of the preceding claims wherein said delustered layer is laminated onto each of the opposite faces of said transparent layer.

5 5. A polyester laminated film according to any one of the preceding claims, wherein said delustered layer is of a biaxially stretched film.

6. A polyester laminated film according to any one of the preceding claims, wherein the amount of the copolymer  
10 composition in the delustered layer is in the range of 1.5 to 10 mol. %.

7. A polyester laminated film according to any one of the preceding claims, wherein the polyester constituting said transparent layer is a polyester which contains ethyl-  
15 ene terephthalate units in an amount at least 98 mol. %.

8. A polyester laminated film according to claim 7, wherein the polyester constituting said transparent layer is a polyester which contains ethylene terephthalate units in an amount at least 99 mol. %.

20 9. A polyester laminated film according to claim 8, wherein the polyester constituting said transparent layer is an ethylene terephthalate homopolymer.

10. A polyester laminated film according to any one of the preceding claims, wherein the polyester constituting  
25 said transparent layer has an intrinsic viscosity higher than 0.45.

11. A polyester laminated film according to claim 10 wherein the polyester constituting said transparent layer has an intrinsic viscosity higher than 0.60.

12. A polyester laminated film according to any one of  
5 the preceding claims wherein the polyester film for the delustered layer has an absolute value  $|\Delta n|$  of birefringence larger than 0.004.

13. A polyester laminated film according to claim 12 wherein the polyester film for the transparent layer has an  
10 absolute value  $|\Delta n|$  of birefringence in the range of 0.004 to 0.2.

14. A polyester laminated film according to any one of the preceding claims wherein said inert inorganic particles are of at least one kind of substance selected from the group  
15 of oxides of inorganic compounds and salts of inorganic compounds, which are inactive with respect to the polyester.

15. A polyester laminated film according to claim 14, wherein said inert inorganic particles are of at least one kind selected from the group consisting of silica, kaolin,  
20 talc, silica alumina, zinc oxide, zinc sulphide, barium oxide, barium sulphate, zirconium oxide, titanium oxide, and calcium carbonate.

16. A polyester laminated film according to claim 15, wherein said inactive particles are of  $\text{SiO}_2$ .

25 17. A polyester laminated film according to any one of the preceding claims, wherein said delustered layer comprises a polyester film containing an anion anti-static agent.

18. A polyester laminated film according to claim 17, wherein the content of said anion anti-static agent is in the range of 0.1 to 10% by weight.

19. A polyester laminated film according to claim 17  
5 or claim 18, wherein said anion anti-static agent is of sodium dodecyl-benzene sulphonate.

20. A polyester laminated film according to any one of the preceding claims wherein the copolymer composition for the delustered layer comprises an ethylene oxide adduct of  
10 bisphenol A.

21. A polyester laminated film according to any one of claims 1 to 19, wherein the copolymer composition for the delustered layer comprises a polyethylene glycol with a molecular weight of less than 6000.

15 22. A polyester laminated film according to any one of claims 1 to 19, wherein the copolymer composition for the delustered layer comprises a triethylene glycol.

23. A polyester laminated film according to any one of the preceding claims wherein said delustered layer has  
20 thickness in the range of 1 to 20 microns.

24. A polyester laminated film according to claim 23 wherein said delustered layer has thickness in the range of 3 to 10 microns.

25. A polyester laminated film according to any one of  
25 the preceding claims wherein said transparent layer has thickness in the range of 10 to 200 microns.

26. A polyester laminated film according to claim 25, wherein said transparent layer has thickness in the range of 15 to 150 microns.

27. A polyester laminated film according to any one of the preceding claims, wherein the stretching ratio thereof in the longitudinal or lateral direction is in the range of 2.5 to 6 times.

5 28. A polyester laminated film according to claim 27 wherein the stretching ratio thereof in the longitudinal or lateral direction is in the range of 2.5 to 4 times.

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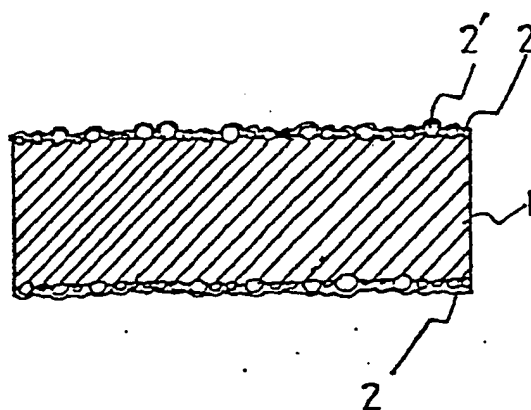


Fig. 1.